have experimented with vacuum tubes in which a fine pencil of cathode rays could be produced. A Wehnelt cathode was formed by melting a small speck of sealing-wax on a fine strip of platinum foil. When the foil was heated to a dull red heat by a current of 5 or 6 ampères, a potential difference of 100 or 200 volts was sufficient to maintain the discharge between the cathode and an aluminium anode placed in a side tube. The slow-moving stream of cathode particles was then subjected to the influence of one pole of a long electromagnet, and the path of the stream observed and photographed. In one tube the magnetic pole was situated in the centre of the spherical bulb through which the stream of electrons passed, in a second tube the pole was placed at any point outside the glass wall of the bulb. The strength of the pole could be increased up to about 1000 C.G.S. units. The spiral paths observed were found to lie on a cone, with its vertex at the magnetic pole.

In conclusion, I desire to express my thanks to Profs. C. G. Barkla and J. B. Dale for their interest in this work, and to the Government Grant Committee of the Royal Society for some of the apparatus employed.

On the Dynamical Nature of the Molecular Systems which emit Spectra of the Banded Type.

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§ 1. *Summary of Paper.*—It is now widely believed, for the reasons recounted in § 2 below, that when the spectrum emitted by a luminous body is of the banded type, the small vibrators which give rise to the radiation are the molecules of the substance, as distinguished from atoms or ions. This result is applied in § 3, which constitutes the main body of the present paper, in order to suggest a dynamical system which is formed of two members in the same way as a diatomic molecule may be supposed to be formed of two atoms, and which has free periods of vibration related to each other by the same formula as holds in the case of banded spectra. This formula presents a certain peculiarity, in that the frequency of vibration occurs in it linearly; whereas in the equation for determining the free periods of dynamical systems in general, the frequency enters by its square. It is shown that from this peculiarity in the radiation of a molecule, certain inferences may be drawn regarding the dynamical character of the connection between the atoms within the molecule, namely, that the kinetic potential of a molecule consists of the kinetic potential of the atoms, together with certain gyroscopic terms: and it is suggested that the exchanges of heat in chemical reactions are due to the necessity for readjusting this gyroscopic energy when the molecules are altered.

In § 4 it is shown that a mechanism somewhat modified from that of § 3 would emit radiations connected by the same law as that which Balmer found for the hydrogen lines.

§ 2. *The Experimental Evidence regarding the Nature of the Vibrators.*—Those spectra which are known to belong to chemical compounds, as distinguished from the elements of which the compounds are composed, are generally of the banded type. This has suggested the hypothesis that banded spectra are produced by molecules, as distinguished from atoms; but as banded spectra are also in certain cases emitted by substances which are chemical elements, it is necessary to examine the question more closely. The elements bromine and iodine, for instance, when excited by a powerful electric discharge, emit spectra which are not banded, but emit banded spectra when the stimulus is less energetic. The banded spectrum may also be obtained reversed as an absorption spectrum, a fact which shows that it is produced by some agent which exists at ordinary temperatures and in the absence of electrical stimulation. These observations suggest that the non-banded spectrum belongs to the element in its most dissociated form, *e.g.*, the atom or ion—while the banded spectrum belongs to the molecular form; and further confirmation of this hypothesis is afforded by the fact that the banded spectrum of bromine vapour is extremely similar to the absorption-spectrum of iodine monochloride; it seems scarcely possible to doubt that, as the molecule I-Cl is the active agent in one case, the molecule Br-Br is the agent in the other. Still further confirmation is afforded by the observation that a temperature so high that the molecules Br_2 and I_2 are dissociated, the banded absorption-spectra are no longer obtained.

Observation of the banded spectra of other chemical elements leads to similar conclusions; thus Graham[*] has been able to distinguish between the absorption-spectrum of sulphur vapour in the form S_2 and that of the vapour in the form S_8.

On the whole, the evidence appears sufficient to justify an attempt to explain the mechanism of the production of banded spectra, on the assumption that the vibrator emitting the radiation is a molecule formed by the combination of chemical atoms.*

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[*] 'Roy. Soc. Proc.,' 1910, A, vol. 84, p. 311.

§ 3. *A dynamical model of the molecule.*—Let us now attempt to design a dynamical model of the molecular vibrator.

The fact that so many properties of chemical substances are of the "additive atomic" kind, leads us to infer that atoms to a considerable extent retain their individuality when they are combined with one another to form molecules; so that a molecule is to be regarded not as a complete rearrangement of the electrons or other elements of which its atoms are composed, but rather as a system in which the atoms exist with comparatively little alteration of their internal structure, but with mutual connections such as may be expressed by additional terms or other modifications in the dynamical equations.

We shall therefore build up our dynamical model from two constituent systems representing the two atoms of a diatomic molecule. For simplicity we shall suppose these atoms to be alike, so that the molecule represented is that of a chemical element.

The position of any point within one of these constituent atoms may be specified by three generalised co-ordinates, which we shall denote by θ, ϕ, ψ. The state, at any instant, of the element of the atom which occupies the position (θ, ϕ, ψ) will be supposed to be specified by a variable u, so that u is a function of θ, ϕ, ψ, and the time t. It would be possible to extend this by assuming that two or three distinct variables u, v, w, are required to specify the state; the principles involved would be the same, and the subsequent analysis and results would be similar though more complicated.

We must now specify the distribution of potential energy within the atom. The simplest assumptions which can be made are that the potential energy of an element of the atom is composed of terms proportional to u^2, or to the squares or products of the first derivates of u with respect to θ, ϕ, or ψ, or to a sum of terms of this kind. That this is so may be seen by considering simple illustrative cases. For instance, suppose that this potential energy is really the electrostatic energy of the charges on a multitude of small conductors contained in the atom (each of these conductors being, say, connected to some other by a perfectly conducting wire having self-induction, so that the charges vary with the time); then it is known that the electrostatic energy of such a system is a quadratic function of the charges; and if we suppose that electrostatic induction is of sensible magnitude only between such conductors as are immediately adjacent to each other, the only terms in the energy which involve a particular charge e_r will be a quadratic combination of e_r, e_{r+i}, $e_{r+j}\ldots$, where e_{r+i}, $e_{r+j}\ldots$ denote the charges on conductors immediately adjacent to e_r. This quadratic combination may be written in the form

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* A dynamical model for banded spectra was described by Sir Joseph Larmor in the article "Radiation" in the supplementary volumes (1902) of the tenth edition of the 'Encyclopædia Britannica.' In this the vibrating system is built up of a large number of constituents, and each line in the spectrum of a constituent gives rise to a band in the spectrum of the entire system.

$$ae_r^2+b\,(e_r-e_{r+i})^2+c\,(e_r-e_{r+j})^2+\ldots,$$

and when we proceed to the limiting case in which the conductors are indefinitely small, indefinitely numerous, and indefinitely close together, and denote the density of charge in a volume-element by u, it is evident that the terms like ae_r^2 will give rise to a term in u^2, while the terms like $b(e_r-e_{r+i})^2$ will give rise to a quadratic function of the first derivates of u with respect to θ, ϕ, and ψ.

In any case, the occurrence of such terms as these in almost all the problems of the vibratory motion of continuous systems which have been investigated will be a sufficient justification for their introduction here.

We shall therefore assume that the potential energy resident in the element $d\theta\, d\phi\, d\psi$ of the first atom at the instant t is

$$\left\{\tfrac{1}{2}ku^2+\tfrac{1}{2}a\left(\frac{\partial u}{\partial\theta}\right)^2+\tfrac{1}{2}b\left(\frac{\partial u}{\partial\phi}\right)^2+\tfrac{1}{2}c\left(\frac{\partial u}{\partial\psi}\right)^2\right.$$
$$\left.+f\frac{\partial u}{\partial\phi}\frac{\partial u}{\partial\psi}+g\frac{\partial u}{\partial\psi}\frac{\partial u}{\partial\theta}+h\frac{\partial u}{\partial\theta}\frac{\partial u}{\partial\phi}\right\}d\theta\, d\phi\, d\psi.$$

In the most general case, the coefficients k, a, b, c, f, g, h, will be functions of θ, ϕ, ψ. We shall adopt the simplest supposition, which is that they are all constant.

The potential energy of an element of the second atom at the instant t will be represented by a similar expression. If (θ', ϕ', ψ') denote a system of generalised co-ordinates suitable for specifying position within the second atom, and if v denote a variable which specifies the state of the element $(d\theta', d\phi', d\psi')$ of this atom at the instant t, the potential energy of this element may be written

$$\left\{\tfrac{1}{2}kv^2+\tfrac{1}{2}a\left(\frac{\partial v}{\partial\theta'}\right)^2+\tfrac{1}{2}b\left(\frac{\partial v}{\partial\phi'}\right)^2+\tfrac{1}{2}c\left(\frac{\partial v}{\partial\psi'}\right)^2\right.$$
$$\left.+f\frac{\partial v}{\partial\phi'}\frac{\partial v}{\partial\psi'}+g\frac{\partial v}{\partial\psi'}\frac{\partial v}{\partial\theta'}+h\frac{\partial v}{\partial\theta'}\frac{\partial v}{\partial\phi'}\right\}d\theta'\, d\phi'\, d\psi'.$$

We have now to consider the nature of the connection between the two atoms. We shall suppose that the systems of generalised co-ordinates (θ, ϕ, ψ) and (θ', ϕ', ψ') are so chosen as to furnish the correlation between the interacting elements of the two atoms, *i.e.*, we shall suppose that the element (θ, ϕ, ψ) of one atom interacts with that element (θ', ϕ', ψ') of the other for which $\theta' = \theta$, $\phi' = \phi$, and $\psi' = \psi$; so that the connection between the atoms can be expressed in terms of the u and v which are functions of the same values of the arguments. We can therefore, in future, make one set of co-ordinates (θ, ϕ, ψ) do duty for both sets.

We may now arrange the permissible types of connections between the atoms in three classes (α), (β), (γ), as follows:—

(α) Such as may be expressed by adding to the kinetic potential terms of the types

$$uv, \quad \frac{\partial u}{\partial \theta}\frac{\partial v}{\partial \theta}, \quad \frac{\partial u}{\partial \phi}\frac{\partial v}{\partial \phi}, \quad \text{etc.,}$$

which do not involve derivates with respect to the time. Terms of this kind would be introduced if, *e.g.*, we supposed that electrostatic induction takes place between the charges in one atom and the charges in the other.

(β) Such as may be expressed by adding to the kinetic potential or Lagrangian function terms of the types

$$\frac{\partial u}{\partial t}\frac{\partial v}{\partial t}, \quad \frac{\partial^2 u}{\partial t \partial \theta}\frac{\partial^2 v}{\partial t \partial \theta}, \quad \text{etc.,}$$

which are products of a derivate of u with respect to the time (and possibly with respect to the co-ordinates also) by a similar derivate of v. Terms of this kind resemble those which represent the mutual induction of electric currents; they would be introduced if, *e.g.*, we supposed that electrokinetic induction takes place between the flux of charge in one atom and the flux of charge in the other.

(γ) Such as may be expressed by adding to the kinetic potential terms of the types

$$u\frac{\partial v}{\partial t}, \quad v\frac{\partial u}{\partial t}, \quad \frac{\partial u}{\partial \theta}\frac{\partial^2 v}{\partial t \partial \theta}, \quad \text{etc.,}$$

in which one of the variables is differentiated with respect to the time and the other is not. Terms of this kind do not generally occur in the kinetic potential of a dynamical system when that function is first written down; but if the system contains "gyroscopic" or "ignorable" co-ordinates, and if these co-ordinates are removed by the process called "ignoration of co-ordinates," terms of this class may be introduced. To suppose that the connection between the two atoms is represented by such terms amounts, therefore, to supposing that the connection is effected by an intermediary agency of the gyroscopic type. It is to be remembered that gyrostatic energy may assume many different physical forms; for instance, an electric current flowing in a closed perfectly conducting circuit, which has self-induction, and also has mutual induction with other non-closed circuits in the system, would be represented by a gyroscopic co-ordinate; and, as Helmholtz showed, the fundamental equations of thermodynamics may be derived on the assumption that heat-energy may be represented by gyroscopic terms.

We have now to decide which of these three possible types of connection (α), (β), (γ), shall be adopted in our model molecule. Terms of the kind (α) and (β) represent the inductive influence which the atoms exert on each other in virtue of their propinquity, and we should naturally choose terms of this kind to represent the connection, if we were to regard a molecule as nothing more than two atoms which are so near as to exert strong mutual inductive influence. But, in spite of that persistency of certain atomic properties to which we have already referred, it is difficult to accept this as an adequate representation of the connection of the atoms in a molecule, when we recall the striking differences which a chemical compound frequently presents from the elements which compose it; and we are led to conclude that, while terms of the kinds (α) and (β) may and probably do exist, they do not represent the dominant feature in the internal economy of the molecule. There remains for consideration the type (γ). If terms of this type occur, the molecule must contain, in addition to the proper internal energy of the atoms, a certain amount of energy of the gyroscopic type, peculiar to the combined or molecular state. That this is the case we may, however, readily believe, for chemical changes, *i.e.*, rearrangements and exchanges of the atoms between molecules, are in general attended by the evolution or absorption of heat; and it seems natural to think of this as the balance left over after the redistribution of gyroscopic energy in the molecules. This idea is further sustained by a closer examination; for connecting terms of the type (γ) in the kinetic potential do not furnish any contribution to the energy, although they influence the motion (just as, *e.g.*, an external magnetic field does not influence the energy of a moving electron, although it causes a deviation of its motion), and the energy of the molecular system therefore consists of the sum of the internal energies of the atoms, together with a constant part, which represents the energy of the gyroscopic connection.

It will be felt to be an argument in favour of this assumption of gyroscopic energy, that it confers a definite individuality on the molecule without destroying the individuality of the atoms of which it is composed, thus enabling us to account at the same time for the persistence of certain properties which are characteristic of the atom, and the appearance of other properties which are characteristic of the molecule.

It may be further remarked that this conception accounts for a polarity of molecules, even of the molecules of chemical elements, such as is suggested by the phenomena of crystals, without assuming that atoms of the same element are different from each other; for such a term as $u\partial v/\partial t$ is unsymmetrical with respect to the two atoms, this term being, in fact, equivalent to $-v\partial u/\partial t$.* The polarity of the molecule is thus represented as a consequence of the connection of the two atoms within it by a gyrostatic link.

Assuming, then, that the connection between the two atoms is represented by a gyrostatic term $lu\,\partial v/\partial t$, and that the inertia of the atoms does not play any important part in the modes of vibration that are to be studied, so that it may be neglected, the kinetic potential of the entire molecule may be represented in the form

$$\begin{aligned}\mathrm{L} = \iiint d\theta\,d\phi\,d\psi\,\Big\{ & \tfrac{1}{2}ku^2 + \tfrac{1}{2}a\left(\frac{\partial u}{\partial\theta}\right)^2 + \tfrac{1}{2}b\left(\frac{\partial u}{\partial\phi}\right)^2 + \tfrac{1}{2}c\left(\frac{\partial u}{\partial\psi}\right)^2 \\ & + f\frac{\partial u}{\partial\phi}\frac{\partial u}{\partial\psi} + g\frac{\partial u}{\partial\psi}\frac{\partial u}{\partial\theta} + h\frac{\partial u}{\partial\theta}\frac{\partial u}{\partial\phi} + \tfrac{1}{2}kv^2 + \tfrac{1}{2}a\left(\frac{\partial v}{\partial\theta}\right)^2 + \tfrac{1}{2}b\left(\frac{\partial v}{\partial\phi}\right)^2 + \tfrac{1}{2}c\left(\frac{\partial v}{\partial\psi}\right)^2 \\ & + f\frac{\partial v}{\partial\phi}\frac{\partial v}{\partial\psi} + g\frac{\partial v}{\partial\psi}\frac{\partial v}{\partial\theta} + h\frac{\partial v}{\partial\theta}\frac{\partial v}{\partial\phi} + lu\frac{\partial v}{\partial t}\Big\},\end{aligned}$$

where k, a, b, c, f, g, h, l denote constants.

The variational equation is

$$\delta\int \mathrm{L}\,dt = 0.$$

Writing this equation *in extenso*, performing the variational operation on each of its terms, integrating by parts so as to obtain δu or δv in each term free from differentiations, and then equating to zero the coefficients of δu and δv in the resulting integrand, we obtain the equations of motion

$$ku - a\frac{\partial^2 u}{\partial\theta^2} - b\frac{\partial^2 u}{\partial\phi^2} - c\frac{\partial^2 u}{\partial\psi^2} - 2f\frac{\partial^2 u}{\partial\phi\,\partial\psi} - 2g\frac{\partial^2 u}{\partial\psi\,\partial\theta} - 2h\frac{\partial^2 u}{\partial\theta\,\partial\phi} + l\frac{\partial v}{\partial t} = 0,$$

$$kv - a\frac{\partial^2 v}{\partial\theta^2} - b\frac{\partial^2 v}{\partial\phi^2} - c\frac{\partial^2 v}{\partial\psi^2} - 2f\frac{\partial^2 v}{\partial\phi\,\partial\psi} - 2g\frac{\partial^2 v}{\partial\psi\,\partial\theta} - 2h\frac{\partial^2 v}{\partial\theta\,\partial\phi} - l\frac{\partial u}{\partial t} = 0.$$

These equations must now be integrated, subject to the boundary conditions. Regarding the latter, the elementary theory of the vibrations of rods, membranes, etc., familiarises us with two kinds of boundary conditions; namely, those exemplified by the vibrations of a straight rod of finite length, in which case there are conditions at the two ends, and those exemplified in the vibrations of an endless rod having a circular form, in which case the condition is that the same physical conditions are to be repeated when the azimuth is increased by 2π. So far as the frequencies of free vibration are concerned, however, these two kinds of boundary-conditions lead ultimately to much the same kind of equation; the latter kind are somewhat simpler, as they require the introduction of fewer symbols; we shall, therefore, take the boundary-conditions in our problem to be of this character, so as to require the solutions of the equations of motion to be periodic functions of θ, ϕ, and ψ, of period 2π. A typical normal oscillation of the system will therefore be represented by the equations

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* For the combination $u\dfrac{\partial v}{\partial t} + v\dfrac{\partial}{\partial t}$ in the kinetic potential, being a perfect differential with respect to t, would furnish no terms in the equations of motion, and therefore $u\,\partial v/\partial t$ is equivalent to $-v\,\partial u/\partial t$.

$$u = \mathrm{A} \sin (nt + p\theta + q\phi + r\psi),$$

$$v = \mathrm{B} \cos (nt + p\theta + q\phi + r\psi),$$

where p, q, r, are integers, and n denotes the frequency.

Substituting these values of u and v in the equations of motion, we have

$$ln\mathrm{B} = (k + ap^2 + bq^2 + cr^2 + 2fqr + 2grp + 2hpq)\,\mathrm{A},$$

$$ln\mathrm{A} = (k + ap^2 + bq^2 + cr^2 + 2fqr + 2grp + 2hpq)\,\mathrm{B}.$$

Eliminating A and B, we have

$$\pm n = k + ap^2 + bq^2 + cr^2 + 2fqr + 2grp + 2hpq,$$

where p, q, r can assume in succession all integer values.

This equation determines the frequency n of the free vibrations of the molecule.

Now according to Deslandres' formula for the frequencies of vibration in a banded spectrum, the frequency of the pth line in the qth band in the rth family of bands is

$$n = p^2 f(q^2, r^2) + \mathrm{B}q^2 + \phi(r^2).$$

This formula of Deslandres may evidently be derived from our analysis if we suppose that the product-terms in the potential energy which have the coefficients f, g, h, are zero, and moreover that the potential energy contains higher derivates such as $\partial^2 u/\partial\theta^2 \times \partial^2 u/\partial\phi^2$, $(\partial^4 u/\partial\phi^4)^2$, etc.; in such assumptions there is nothing unnatural.

Some writers do not accept Deslandres' formula, asserting that the banded spectra are better represented if terms involving the first and other odd powers of p, q, r, are included in the empirical formula. If so, the terms in f, g, h, above should be retained. The equation, in fact, has a considerable adaptability consistent with the retention of its cardinal feature, which is that the frequency (*not* the square of the frequency, which is the quantity usually occurring in such equations derived from dynamical systems) is expressed as a simple function of three quantities, p, q, r, which are to assume in succession all integer values. This cardinal feature of the frequency-equation is derived from the cardinal feature of the model, which is the union of two atoms within a molecule by a connection of the gyrostatic type.

§ 4. *The Series Spectrum of Hydrogen.*—It may be not without interest to add that it is possible on these principles to construct a vibrator whose free periods are those of the series spectrum of hydrogen.

We have only to postulate two similar constituents in the vibrator, the potential energy of the one being

$$\tfrac{1}{2}au^2+\tfrac{1}{2}b\left(\frac{\partial u}{\partial\theta}\right)^2,$$

and of the other being

$$\tfrac{1}{2}av^2+\tfrac{1}{2}b\left(\frac{\partial v}{\partial\theta}\right)^2,$$

the two constituents being joined by a connection of the gyroscopic type, which after ignoration gives rise to a term

$$\frac{\partial u}{\partial\theta}\frac{\partial^2 v}{\partial t\,\partial\theta}$$

in the kinetic potential. This resembles the term introduced in the case of the banded spectra, differing from it only in that the derivates $\partial u/\partial\theta$ and $\partial v/\partial\theta$ replace u and v. The variational equation is now

$$0=\delta\iint dt\,d\theta\left\{\tfrac{1}{2}au^2+\tfrac{1}{2}b\left(\frac{\partial u}{\partial\theta}\right)^2+\tfrac{1}{2}av^2+\tfrac{1}{2}b\left(\frac{\partial v}{\partial\theta}\right)^2+\frac{\partial u}{\partial\theta}\frac{\partial^2 v}{\partial t\,\partial\theta}\right\},$$

which gives the equations of motion

$$au-b\frac{\partial^2 u}{\partial\theta^2}-\frac{\partial^3 v}{\partial t\,\partial\theta^2}=0,$$

$$av-b\frac{\partial^2 v}{\partial\theta^2}+\frac{\partial^3 u}{\partial t\,\partial\theta^2}=0.$$

We assume that each constituent is ring-shaped, so that it returns into itself when θ increases by 2π. A normal free oscillation will therefore be represented by

$$u=\mathrm{A}\sin(nt+m\theta),$$

$$v=\mathrm{B}\cos(nt+m\theta),$$

where m denotes an integer and n denotes the frequency of vibration. Substituting these values in the equations of motion, we have

$$(a+m^2b)\,\mathrm{A}=m^2n\mathrm{B},$$

$$(a+m^2b)\,\mathrm{B}=m^2n\mathrm{A},$$

so the equation which determines the frequencies of vibration is

$$\pm n=b+\frac{a}{m^2},$$

as in the hydrogen spectrum.